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MEANS FOR AND METHOD OF PRODUCING ALUMINUM

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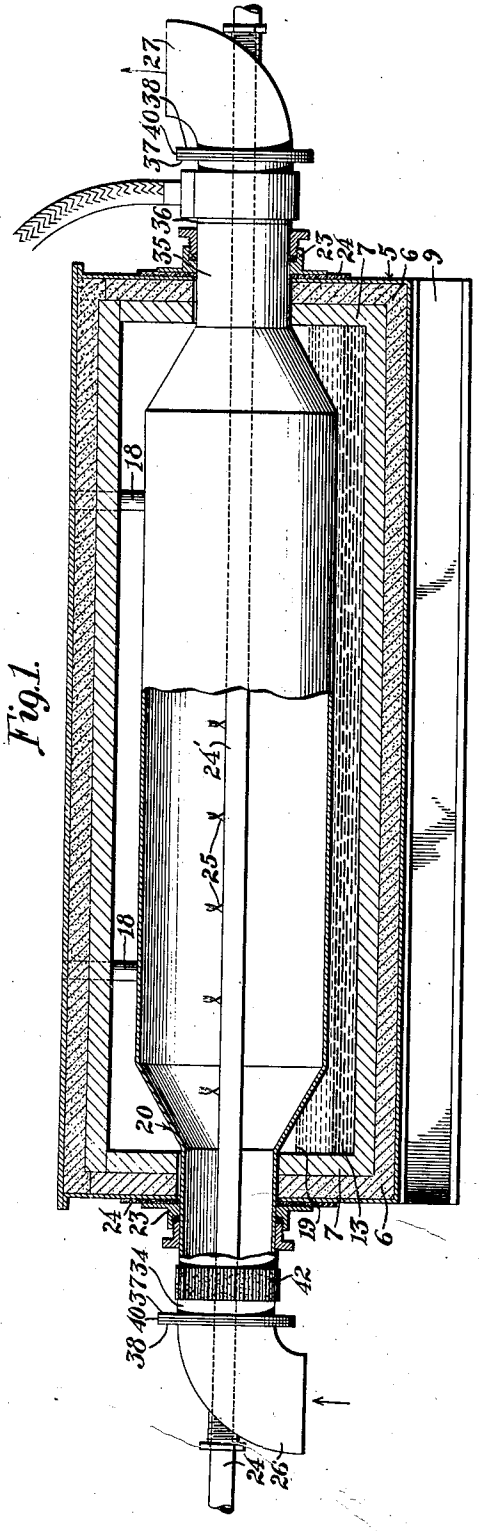


Fig. 1.

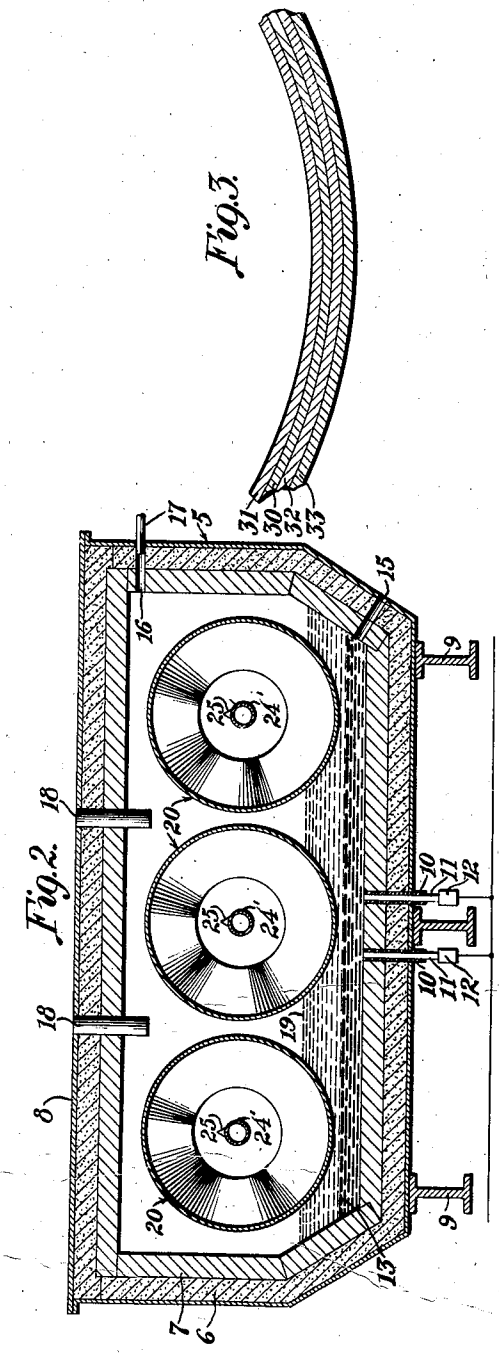


Fig. 2.

Fig. 3.

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MEANS FOR AND METHOD OF PRODUCING ALUMINUM

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19 Claims. (Cl. 204—20)

The present invention relates to means for and a method of producing aluminum and more particularly to an improved electrolytic cell, a substantially indestructible anode for use in the production of aluminum, an improved electrolytic bath for aluminum oxide and a method of producing aluminum therefrom.

Heretofore in the production of aluminum a molten electrolyte has been used consisting of a solution of oxide of aluminum, alumina, in cryolite. The composition of the bath has been so regulated that in the molten state the specific gravity thereof is somewhat less than the specific gravity of molten aluminum and consequently the molten metal remains below the fused electrolyte at the bottom of the container and remains as molten aluminum which serves as the cathode of the electrolytic cell. The temperature of the electrolytic bath has been kept as low as possible, and in normal operation is about 1000° C. During electrolysis of the alumina dissolved in the fused cryolite, aluminum is liberated in the molten state at the cathode and oxygen is liberated at the anode which comprise carbon electrodes immersed in the molten electrolyte. The electrolytic bath is covered with a coating which is usually finely divided carbon in order to decrease the heat loss. However, a substantial portion of the carbon electrodes is consumed by the oxygen liberated at their surface whereby the electrodes are caused to waste away quite rapidly. This wasting away disarranges the electrical circuit and requires hand manipulation of electrodes to compensate for shortening thereof. Other disadvantages such as contamination of aluminum by ash of the electrodes are also encountered.

Due to the quantity of carbon in the bath and below the aluminum cathode as lining of the cell, quantities of aluminum carbide form and float up to the top of the bath and are changed back to aluminum oxide and an oxide of carbon thus necessitating further electrolytic reduction of the aluminum oxide so formed. The reduction of this additional quantity of oxide, without the production of commensurate quantities of aluminum, increases the energy consumption per unit of metal deposited. Further, since the carbon electrodes or anodes waste away at a non-uniform rate, the distance between the cathode and any carbon anode is not always the same and therefore the distance between the anode and cathode is dependent upon such wasting away and the non-uniformity in distance therebetween creates a greater resistance opposed to the passage of the current and therefore increases the cost per unit of metal produced.

The present invention provides an electrolytic bath, the melting point of which is substantially less than the melting point of baths now in use whereby the loss of electrolyte by volatilization is substantially reduced. The invention also provides an electrolytic bath which is water thin at temperatures in the neighborhood of 760° C. and the specific gravity of which is about 2.11 and therefore less than the specific gravity of molten aluminum at the same temperature. This bath mixture contains sufficient alumina from which the metallic aluminum can be obtained by electrolysis.

An improved container or cell is provided for the electrolytic operation and the cell is provided with heat insulating material provided upon all sides of the cell to prevent loss of heat through the cell walls and thereby decrease the consumption of electric energy in the production of a unit of metal which material brings no carbon into contact with aluminum and thus produces carbon free aluminum.

The invention further provides a method of and apparatus for the production of metallic aluminum in which the molten electrolytic bath is not contaminated with carbonaceous materials and in which the surface of the bath is not covered with a layer of carbon and consequently oxygen liberated at the anode may be recovered in pure and uncontaminated form and not accompanied by quantities of oxides of carbon. The anode, provided by my invention, comprises electrodes which are resistant to the attack of oxygen or fluorine at the temperatures obtaining in the bath and which are also resistant to the action of the materials of the bath.

My improved anode comprises a hollow rotatable electrode which is adapted to transmit heat to the electrolytic bath to aid in maintaining the bath in a molten condition, and to this end a substantially large surface of the anode has contact with the bath.

The invention also provides means for agitating the molten bath to maintain a substantially equal distribution of the constituents throughout the bath as the electrolysis proceeds and to incorporate added alumina therein. A hollow, rotatable, relatively indestructible anode is probided by the invention in which a combustible charge can be burned and the heat of the combustion transmitted through the walls of the electrode to the electrolytic bath to aid in maintaining the bath in a molten condition.

The invention, therefore, provides an electrode the inner walls of which are made of a material to withstand the action of a combustible charge and of products of the combustion, the outer surfaces of which are formed of material to withstand the destructive action of oxygen liberated at the anode and to withstand the action of the constituents of the bath itself. The invention also provides a heat interchanger in the form of an anode for regulating the temperature of the electrolytic bath.

In the drawing:

Fig. 1 represents a longitudinal vertical section showing the heat insulated bath, the rotatable anode and the means for introducing the combustible charge into the anode.

Fig. 2 is a cross section of a bath showing a plurality of anodes and showing with more particularity the means by which electrical contact is made with the cathode.

Fig. 3 is an enlarged fragmentary section of an anode wherein the inner and outer lining materials are plainly shown.

Referring more particularly to the drawing the casing of an electrolytic cell or container is shown generally at 5 and may be of any suitable composition, as for instance, steel sheets. The inner surface of the sheets is provided with a heat insulating lining 6 preferably of powdered alumina over which is placed an additional layer of insulating material 7 comprising slabs of fused aluminum oxide. The cell is provided with a cover portion 8 which is also provided with heat insulation of a type similar to that used upon the bottom and side walls of the cell, whereby the completed and operating cell will retain the maximum quantity of heat contained within the walls thereof and the losses by radiation be reduced to a substantial minimum.

The cell itself may be supported upon suitable supports such as the I beams 9 or, under some conditions of operation, may be placed directly upon the floor of the cell room. The cell is provided with suitable insulating sleeves, as at 10 projecting through the bottom of the cell by means of which electrical contact is made with the cathode 13 of the cell which at the temperatures of operation is molten aluminum. I propose to use sleeves of "alundum" in which frozen aluminum metal 11 acts as terminal contacts for the cathode having electrical contact with suitable bus bars or main current lines 12.

Provision is made adjacent the bottom of the cell for drawing off molten aluminum, preferably at a constant rate, and a rate which is substantially equivalent to the rate of deposition of the metal although the operation can be practiced intermittently. To this end, a suitable offtake is positioned in the side wall of the cell adjacent the bottom thereof, as at 15. Another exit is provided in a wall of the cell to permit the withdrawal of the other products formed by the electrolysis of the alumina, to wit, oxygen. This withdrawal port 16 is placed in the side wall of the cell adjacent the top cover thereof and as this product is liberated in substantially pure state, provision is made for collecting and storing this element, and in general, the exit pipe 17 leads to a convenient storage tank or compressor.

As will be made more apparent, the product which is electrolyzed, alumina, is continuously decomposed during the process of the electrolysis and I propose to add additional quantities of alumina to the bath to maintain the composition of the bath at the desirable concentration pointed out in detail hereinafter. This gradual addition of alumina becomes important since certain constituents of the bath, for instance cryolite is, in fused condition, a solvent for the heat insulating material placed upon the inner walls of the cell or container. It, therefore, becomes of importance to maintain a saturated condition in the bath with respect to the alumina. To this end charging ports 18 are formed in the cover 8 through which additions of alumina may be made, preferably at a constant rate, by suitable automatic mechanism of conventional type.

Further, since I desire to maintain the melting point or fusion point of the bath at a desirably low point, I find it advantageous to add alumina continuously to the bath at a rate which is substantially equal to that at which the bath is depleted in this product. A preferable composition of the bath comprises 5.50 grams of cryolite for each 13.92 grams of potassium fluoride (dehydrated), and 2.0 grams of lithium fluoride to which 1.0 gram of aluminum oxide has been added. The melting point of this particular mixture, that is, 24.5% cryolite, 62.1% potassium fluoride, 8.9% lithium fluoride and 4.5% alumina is 760° C., and from my experiments I believe it to be the lowest melting point mixture of cryolite, lithium fluoride, potassium fluoride and alumina and therefore represents a mixture in the nature of an eutectic mixture. In practice, the quantities may be varied over a range wherein the melting point of potassium fluoride, cryolite mixture varies from about 760° C. to about 800° C.

As mentioned hereinabove, by maintaining the bath saturated with alumina the walls of the electrolytic cell are protected from the solvent action of the bath. In order to maintain a substantially homogeneous composition throughout the bath, to prevent depletion of alumina at the electrode surfaces and at the points of contact with the walls of the bath, means are provided for slowly agitating and mixing the molten materials.

In the structure illustrated in the drawing, a rotatable anode 20 is suspended in the bath and when rotated produces sufficient agitation thereof to maintain a substantially homogeneous composition therethrough. The anode also serves as a heat interchanger to aid in maintaining the temperature of the bath at a sufficient degree and at a substantially static point, i. e. between about 760° C and 800° C. Depending upon the current density used in the electrolysis and the size of electrolytic furnace and its heat insulation, the anode may be used to either furnish heat by burning the combustible material within the anode or at greater electric intensity heat may be dissipated through the anode walls to a cooling fluid to maintain the static temperature condition in the bath. In Fig. 1 of the drawing the hollow electrode 20 is suspended horizontally in the bath and to a point as close as praticable to the cathode 13, but not so close that contact of the anode and cathode occurs, or that short circuiting is produced, or that the metallic portions of the cathode will alloy with the anode material. In practical operations the clearance between the anode and cathode is on the order of a half centimeter; such proximity insures a substantially low bath resistance and thus decreases the energy outlay in the production of aluminum.

The hollow electrodes 20, extending through openings in the side walls of the cell or container, are largely floated by the bath and supported loosely upon the electrically insulated

glands 23 attached to the side walls of the cell and are normally insulated from the cell casing by the insulation ring 24. The height of the bath within the cell is so regulated that the surface 19 of the bath is lower than the bearing surfaces of the anode and the glands 23 in order to prevent escape of oxygen between the anode and cell wall with consequent loss of material from the cell or fusion of the constituents of the bath between the anode and the gland. A ring gear 42 of insulating material is attached to a protruding end 34 of anode 20 for engagement with a power shaft whereby the anode can be rotated at any desirable rate.

Provision is made whereby a combustible mixture may be led into the hollow anode and united therein in such fashion that the heat liberated by such combustion may be carried to the outer walls of the hollow anode by convection, conduction, and radiation and be transmitted through the walls of the anode to the bath. To this end, the form of the invention shown in the drawing is provided with intake pipes 24' through which combustible material of any desired type, either powdered, solid, liquid, or gaseous fuel may be led and be discharged through convenient jets 25 into the interior of the anode and there come in contact with and unite with a desirable supporter of combustion such as air or oxygen. The supporter of combustion, which is desirably preheated, is conducted into the interior of the anode through the elbow connection 26 and unite with the combustible substances issuing from the jets 25, a portion of the heat so liberated being conducted to the bath as aforesaid.

The products of the combustion are withdrawn from the interior of the anode and discharged through the elbow 27 preferably through a conventional checker work or regenerator system before being discharged to the stack. It is to be noted that by the use of a checker work or regenerator, the air or oxygen used to support the combustion of the combustible material may be pre-heated before entrance into the hollow anode and thus further aid in effecting a substantially complete energy recovery. Where the exhaust products of combustion are passed through a regenerator and air is passed through the pre-heater or regenerator prior to its entrance into the combustion chamber, such entering air is at a temperature of about 400° C. and the temperature upon the interior of the anode is in the neighborhood of 800° C.

The core of the anode, Fig. 3, comprises a metal capable of withstanding the extreme temperatures of the bath and which in addition is a relatively good conductor of heat and electricity as for instance a steel cylinder. In order to prevent excessive corrosion and decomposition of the anode, I coat the interior of the steel core 30 with a deposit of nickel 31 which is on the order of $\frac{1}{32}$ of an inch in thickness or better. After the deposition of the nickel the coated steel is rolled in order to produce a substantially coherent and non-porous coating upon the inner surface. In order to prevent excessive decomposition of the outer surface, the outer surface of the steel anode is steamed at a temperature sufficient to form magnetic oxide of iron, that is, at temperatures above about 500° C.

The magnetic oxide layer 32 is further protected by a deposit of silver 33 on the order of $\frac{1}{32}$ of an inch or more in thickness. This surface is rolled in sheets to obtain the proper coherence of the silver layer. The layer of silver is sufficiently porous to permit a slow diffusion of oxygen therethrough at the temperatures of the bath, that is, from about 750° C. to about 800° C.; it does not combine with oxygen at this temperature and is sufficiently dense to prevent passage of liquid constituents of the bath through it. The reduced ends or extremities 34 and 35 of the anode protrude through the side walls of the electrolytic cell and an end 35 makes connection with the source of current. This end is preferably coated with an electrically conducting material, as for instance a copper sheet 36, which contacts with the electric contact member 37 which leads from a suitable source of current.

The inlet and exit pipes 26 and 27 are provided with flanged portions 38 for abutment with insulating rings 40 upon companion flanged portions 37 of the extremities of the hollow anode whereby a sufficiently close joint is provided to prevent entrance or loss of any considerable quantity of combustible material or products of combustion. Normally, the stack pressure upon the system will be sufficient to insure a slight leakage of air between these joints, the quantity of which is insufficient to materially affect efficient operation of the process.

Although it has been indicated in the foregoing description that heat is added to the electrolytic bath by burning combustible material within the hollow anode 20, my invention contemplates another mode of operation under operating conditions where excessive amounts of heat are generated by passage of the electric current through the bath. When it is desired to increase the output of the individual cell, the number of amperes flowing through the cell is increased thus increasing the amount of heat generated in the bath by the passage of current between the anode 20 and cathode 13. When current on the order of 15,000–20,000 amperes per anode is used, large quantities of heat are generated and strong convection currents are set up in the bath aiding in the mixing action whereby the added alumina is uniformly distributed and dissolved in the electrolytic solvent of cryolite, lithium fluoride and potassium fluoride.

To prevent the temperature of the bath from rising to a point where certain of the constituents thereof are appreciably volatile, I propose to conduct a cooling fluid through the hollow anode 20 and extract the excess heat from the bath and thus maintain the temperature thereof in the neighborhood of the range 760° C. to 800° C.

In many localities desirable working conditions will include the use of so-called "off peak power" and my invention can be used advantageously by employing the anode described herein as a temperature stabilizer. Thus, where the electrolysis is performed as an intermittent operation with "off peak power", in contradistinction to a continuous operation, the anode can be heated by burning combustible material therewithin in order to prevent the freezing of the bath to a hard stone-like substance which would cause damage to the interior of the cell, until such time as the power is again available when normal operation can be resumed.

During all conditions of operation of the cell,

I contemplate maintaining a proper temperature control within very close limits and such operation may be carried out due to the fact that the anode is substantially indestructible. It is possible to maintain such temperature control by means of a suitable thermocouple, as for instance a couple composed of a platinum and ninety percent platinum, ten percent rhodium couple immersed in the bath at some convenient portion and connected with lead wires to a suitable potentiometer. By employing the temperature stabilizing condition in conjunction with proper temperature control with an anode composed of materials which comprise the best electrical conductors known and the proper design of the electrolytic cell such as described herein, large outputs can be maintained with a consequent decrease in cost of metal produced which is not the case where the anode is constantly wasted away and hand manipulation resorted to to compensate for this destruction. I therefore contemplate handling large currents per electrode, as for instance in the neighborhood of fifteen to twenty thousand amperes or more and the furnace can be supplied with a number of electrodes connected in parallel.

As the resistance of the bath is a large item of the electrical circuit, much heat is set up by the passage of this large current and with the cell sufficiently well heat insulated as described, a rise of temperature will show itself upon the pyrometer. Conditions of operation and the design of the furnace will therefore determine what office the anode will serve in the matter of a stabilizer of temperature. In a small furnace, combustibles will be burned within the anode to supply heat thereto in order to maintain the correct temperature of the bath while in a furnace or cell of large capacity it will be found desirable to abstract heat from the furnace during the more vigorous and increased electrolytic action. This can be done by passing a cooling medium through the anode when the temperature of the bath rises to maintain the temperature within a very close limit, as for instance between the 750° C. to 800° C. as mentioned above.

Although I have found that the composition of baths mentioned above seems a desirable composition for use wherein the electrolyte comprises 13.92 grams potassium fluoride, 5.50 grams cryolite, for each two grams of lithium fluoride, during the course of my experiments I have found that when 3.5 grams cryolite and 13.92 grams potassium fluoride were mixed together and heated a clear fluid was obtained at about 820° C. The addition of one gram of lithium fluoride made the bath somewhat more fluid and this bath could be melted at 760° C. Upon addition of one gram of aluminum oxide, however, very little solubility was incurred at these lower temperatures and at a temperature of 850° C. the bath contained quantities of undissolved floating material.

At higher temperatures the bath cleared up. In another experiment with lithium fluoride and cryolite 6.24 grams of lithium fluoride and 5.50 grams of cryolite were heated together and the material melted at approximately 710° C. However, this bath contained very little solvent power for aluminum oxide at the lower temperatures and in order to obtain solubility the temperature had to be increased in the neighborhood of or considerably above 850° C.

When, however, 5.5 grams of cryolite were mixed with 13.92 grams of potassium fluoride and one gram of lithium fluoride a bath was obtained which melted between 760° C. and 780° C. which had a certain amount of fluidity at that temperature and which dissolved aluminum oxide to a moderate degree. Upon increasing the amount of lithium fluoride to two grams the fluidity of the bath was found to be increased and the solvent action of the bath for aluminum oxide more rapid. This bath was found to give good results from the point of view of rapidity of solution of aluminum oxide, fluidity of bath and low fusion temperature since the bath was perfectly clear and mobile and water thin at a temperature of 760° C. The specific gravity of this bath, as determined at a temperature of about 800° C. was 2.11 and so that the bath would float upon molten aluminum at the same temperature.

It is to be particularly pointed out that the present invention provides a substantially indestructible anode and one in which loss due to the resistance offered to the passage of the current is at a minimum. The coating of silver provides a relatively indestructible electrode, one which is a good conductor of heat and electricity, one which is unaffected by the chemical action of the constituents of the fused and molten bath, an electrode which is solid at the temperature of the bath, and an electrode unaffected by oxygen or fluorines.

Further, the temperature at which the electrolysis takes place is sufficiently low to prevent excessive volatilization of potassium fluoride in the bath and in this respect the process differs materially from the process as currently in use where bath temperatures of 1,000° C. and upward are not uncommon and wherein appreciable loss of the bath constituents are suffered due to vaporization.

What is claimed is:

1. The method of depositing aluminum electrolytically which comprises passing electric energy through a molten electrolytic bath containing alumina at a temperature below 800° C. thereby depositing aluminum at a cathode of molten aluminum below the level of the molten bath and liberating oxygen at the surface of a rotating anode which resists the action of oxygen.

2. The method of depositing aluminum electrolytically which comprises passing electric energy through a molten electrolytic bath and adding heat energy to the bath to aid in maintaining the molten condition thereof by burning a combustible charge in the interior of a hollow anode.

3. The method of depositing aluminum electrolytically which comprises passing electric energy through a molten electrolytic bath and adding heat energy to the bath to aid in maintaining the molten condition thereof by rotating a hollow anode in contact with the bath but spaced from the molten aluminum below the bath and burning a combustible charge in the interior of the anode.

4. The method of depositing aluminum electrolytically which comprises passing electric energy through a molten bath containing alumina, thereby depositing aluminum at the cathode, adding heat energy to the bath to aid in maintaining the molten condition thereof by burning a combustible charge in the interior of a hollow anode, and rotating the anode in the bath.

5. The method of depositing aluminum electrolytically which comprises passing electric energy through a molten bath containing about 62.0% potassium fluoride, 24.0% cryolite, 9% lithium fluoride, 5% alumina, adding heat energy to the

bath to aid in maintaining it in a molten condition by burning a combustible charge in the interior of a hollow anode, and protecting the anode from the action of the oxygen of the constituents of the bath by a coating upon the exterior of the anode which resists the action of oxygen.

6. The method of depositing aluminum electrolytically which comprises passing electric energy through a molten bath containing about 62.0% potassium fluoride, 24.0% cryolite, 9% lithium fluoride, and 5% alumina, adding heat energy to the bath to aid in maintaining it in a molten condition by burning a combustible charge in the interior of a hollow anode, and protecting the anode from the action of the oxygen and the constituents of the bath by a coating of silver upon the exterior of the anode.

7. The method of depositing aluminum electrolytically which comprises passing electric energy through a molten bath containing about 62.0% potassium fluoride, 24.0% cryolite, 9% lithium fluoride, and 5% alumina, adding heat energy to the bath to aid in maintaining it in a molten condition by burning a combustible charge in the interior of a hollow anode, and protecting the anode from the action of the oxygen of the constituents of the bath, and a coating upon the interior of the anode to protect the same from the action of the combustible charge and the products of the combustion.

8. The method of depositing aluminum electrolytically which comprises passing electric energy through a molten bath containing about 62.0% potassium fluoride, 24.0% cryolite, 9% lithium fluoride and 5% alumina, adding heat energy to the bath to aid in maintaining it in a molten condition by burning a combustible charge in the interior of a hollow anode, and protecting the anode from the action of the oxygen of the constituents of the bath, and a coating of nickel upon the interior of the anode to protect the same from the action of the combustible charge and the products of the combustion.

9. The method of depositing aluminum electrolytically which comprises passing electrical energy through a molten electrolytic bath containing alumina at a temperature below 800° C. thereby depositing aluminum at a cathode of molten aluminum below the surface of the bath, maintaining the temperature of the bath below 800° C. by heat interchange through the heat conducting walls of an anode, and circulating a fluid in said anode.

10. A composition suitable for use as an electrolytic bath for the production of aluminum comprising about 62.0% potassium fluoride, 24.0% cryolite, 9.0% lithium fluoride and 5% alumina.

11. A composition suitable for use as an electrolytic bath for the production of aluminum containing about 62.0% potassium fluoride and 9.0% lithium fluoride in addition to cryolite and alumina to saturation and melting in the neighborhood of 760° C. to a water thin liquid with weight of 2.11 grams per cubic centimeter at about 800° C.

12. An electrolytic cell for the production of aluminum comprising an electrolytic bath containing alumina having a melting point below that of silver, a cathode of aluminum beneath said bath, and a rotatable metallic anode positioned horizontally in said bath.

13. An electrolytic cell for the production of aluminum comprising an electrolytic bath containing alumina having a melting point below that of silver, a cathode of aluminum beneath said bath, and a hollow metallic anode positioned horizontally in said bath.

14. An electrolytic cell for the production of aluminum comprising an electrolytic bath containing alumina having a melting point below that of silver, a cathode of aluminum beneath said bath, and a hollow rotatable metallic anode positioned horizontally in said bath.

15. An electrolytic cell for the production of aluminum comprising an electrolytic bath containing alumina having a melting point below that of silver, a cathode of aluminum beneath said bath, and a hollow rotatable anode covered with a metal substantially inert toward oxygen at the temperature of operation of the cell.

16. An electrolytic cell for the production of aluminum comprising an electrolytic bath containing alumina having a melting point below that of silver, a cathode of aluminum beneath said bath, and an anode coated with silver.

17. An electrolytic cell for the production of aluminum comprising an electrolytic bath containing alumina having a melting point below that of silver, a cathode of aluminum beneath said bath, and a hollow metallic anode coated with silver upon the portions of the anode in contact with the bath and with nickel upon the inner portions of the anode.

18. The method of depositing aluminum electrolytically from a fused bath containing alumina which comprises adding heat energy to the bath to maintain the same in a molten condition, passing electrical energy through said bath whereby aluminum is deposited at a cathode of molten aluminum below the surface of the molten bath and liberating oxygen at the surface of an indestructible anode having a melting point above that of the temperature of the molten bath and rotating said anode.

19. A composition suitable for use as an electrolytic bath for the production of aluminum comprising cryolite, potassium fluoride, alumina and lithium fluoride, the resultant bath having a freezing point below 800° C.

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